

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C09D 11/00	A1	(11) International Publication Number: WO 00/63305 (43) International Publication Date: 26 October 2000 (26.10.00)
(21) International Application Number: PCT/US00/10078 (22) International Filing Date: 14 April 2000 (14.04.00) (30) Priority Data: 60/129,691 16 April 1999 (16.04.99) US (71) Applicant: GEM GRAVURE COMPANY, INC. [US/US]; 112 School Street, West Hanover, MA 02339 (US). (72) Inventors: SITARAM, Srinivas, P.; 2602 Village Road West, Norwood, MA 02062 (US). MCHUGH, Olena; 360 East Street, Hingham, MA 02043 (US). GEMELLI, David, J.; 607 Broadway, Hanover, MA 02339 (US). ELMER, Rick, Allen; 3926 West Vicki Place, Brookline, MO 65619 (US). (74) Agents: PIERCE, N., Scott et al.; Hamilton, Brook, Smith & Reynolds, P.C., Two Militia Drive, Lexington, MA 02421 (US).		(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: NON-SETTLING AND STABLE OPAQUE PIGMENTED INK-JET INK (57) Abstract An ink-jet ink includes: a colorant selected from the group consisting of Pigment Orange 16 and Pigment Orange 64; a dispersant selected from the group consisting of polymeric hyperdispersants and polymeric dispersing agents with pigment-affinic groups; a polymer; and a solvent.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

NON-SETTLING AND STABLE OPAQUE PIGMENTED INK-JET INK

BACKGROUND OF THE INVENTION

Ink-jet printing is a non-contact method of printing in which droplets of ink are produced and directed through at least one orifice onto a substrate. Ink-jet printing can be subdivided into two general technology groups; continuous ink-jet printing and drop-on-demand ink-jet printing. In continuous ink-jet printing, the ink droplets are produced continuously. A charge is applied to the ink droplets, which then are deflected through an electrostatic field. The charged droplets are either controlled to return to the ink chamber through a gutter return system or are directed onto a specific location on a moving substrate. In drop-on-demand ink-jet printing, droplets of inks are not charged and are formed or expelled from the orifice when required for printing on the moving substrate.

Ink-jet ink compositions must meet certain requirements to work reliably in ink-jet printers. These properties relate to viscosity, solubility, surface tension, and compatibility of components. Further, the ink must be quick-drying and capable of producing a clear and distinct image on the substrate. For use in continuous ink printers, ink compositions require sufficient conductivity for reliable ink droplet charging.

Traditionally, white pigmented ink-jet inks, based on titanium dioxide have been used to print onto black substrates. These inks can settle over a period of time, leading to poor ink shelf life and the clogging of the ink-jet nozzles, when run in the printer. Titanium dioxide based ink-jet inks can be used only in ink-jet printers, which are fitted with a mechanical mechanism for keeping the white pigment suspended. These particular inks cannot be used in dye-based continuous ink-jet printers or drop-on-demand printers, where there is no mechanical means of keeping the pigment suspended. It is a desired benefit for ink-jet printing to have universal colored opaque ink to print onto both white and black substrates. This will allow customers to use one ink to print onto a wide variety of colored substrates without having the need to remove or swap inks from the ink-jet printer. White opaque ink-jet ink compositions will not show up clearly on white substrates. Yellow opaque

and light blue opaque ink-jet ink compositions are currently available in the market places. These inks often either do not run reliably in ink-jet printers, or they contain titanium dioxide in addition to the yellow or blue colorant and so will be requiring an external mechanism in the ink-jet printer to keep the white pigment suspended or
5 they do not provide sufficient opacity on both white and black substrates.

The objective of this invention is to provide a more improved and reliable pigmented ink composition, suitable for use in ink-jet printers to provide opaque images. A second objective of this invention is to produce a robust orange pigmented ink to run reliably in an ink-jet printer. Another objective of this
10 invention is to produce an opaque pigmented ink, that has good shelf life and stability. A further objective of this invention is to produce an opaque ink composition, which is non-settling and can be used in ink-jet printers, which do not employ a mechanical device to keep the pigment in the ink suspended. Yet another objective is to produce a robust reliable ink-jet ink composition, which has good
15 shelf life stability and good adhesion to porous and non-porous substrates.

SUMMARY OF THE INVENTION

The invention relates to an ink-jet ink. The ink-jet ink includes: a colorant selected from the group consisting of Pigment Orange 16 and Pigment Orange 64; a dispersant selected from the group consisting of polymeric hyperdispersants and
20 polymeric dispersants with pigment-affinic groups; a polymer; and a solvent.

The present invention provides a non-settling ink suitable for use in ink-jet printers for printing opaque images onto both white and black substrates. An advantage of the ink in this invention is that it has an extended shelf life and can be used reliably in both opaque and non-opaque ink-jet printers and does not lead to the
25 clogging of nozzles or the blockage of the filters fitted in the ink systems of ink-jet printing systems.

DETAILED DESCRIPTION OF THE INVENTION

A description of preferred embodiments of the invention follows.

The ink-jet composition of the present invention includes a solvent, a pigment selected from the group consisting of Pigment Orange 16 and Pigment
5 Orange 64, a dispersant selected from the group consisting of polymeric hyperdispersants and polymeric dispersing agents with pigment-affinic groups, and a polymer. In addition, the formulation may include a conductivity agent, other additives and additional colorants. The choice of materials is wide and will depend on the application and properties required.

10 Solvents suitable for the enclosed invention include diacetone alcohol, methoxy propyl acetate, 2-pyrrolidinones and the like, substituted pyrrolidinones such as N-methyl pyrrolidinone and the like, ketones such as acetone, methyl isobutyl ketone, methyl ketone, diethyl ketone, cyclohexanone and the like, esters such as ethyl acetate, butyl acetate, methyl acetate, tertiary butyl acetate and the like,
15 lactates such as butyl lactate, ethyl lactate and the like, alcohols such as methanol, ethanol, n-butanol, n-propanol, isopropanol and the like, hydrocarbon solvents such as hexane, cyclohexane and the like, glycols such as ethylene glycol, propylene glycol and the like, glycol ethers such as ethylene glycol dimethyl ether, ethylene glycol diethylether, a dialkylether of ethylene glycol, CELLOSOLVE, diethylene
20 glycol dimethylether, diethylene glycol diethylether, lactones, sulfones, water and the other solvents commonly known to one skilled in the art. Methyl ethyl ketone is a preferred solvent. If desired, a mixture of solvents can be employed.

The ink composition includes a colorant selected from the group consisting of Pigment Orange 16 and Pigment Orange 64. Any orange, red or brown opaque
25 pigment also may be employed in the present invention. Examples of other pigments suitable for use in the present invention include, but are not limited to, the pigments Pigment Orange 34, Pigment Orange 36, Pigment Orange 61, Pigment Orange 62, orange pigments containing nickel, Pigment Red 254, Pigment Red 255, and Pigment Brown 5. If desired, a mixture of pigments and dyes, which dissolve in
30 the ink composition, can be used to modify the final color of the ink. Preferred

pigments are Pigment Red 254, Pigment Red 255 and orange pigments based on nickel.

The pigments added to the ink either are dispersed with a dispersant selected from the group consisting of polymeric hyperdispersants and polymeric dispersing agents with pigment-affinic groups. If desired, a mixture of polymeric hyperdispersants, polymeric dispersants with pigment-affinic groups and polymers may be used. Suitable polymers include vinyl acetate vinyl chloride copolymers; vinyl acetate vinyl chloride terpolymers; urea aldehyde resins; polyketone resins; polyester resins; acrylic resins; styrene acrylic resins; polyurethanes; phenol-based resins; cellulose-based resins, including cellulose nitrate, cellulose acetate butyrate. Urea aldehyde resins and vinyl acetate vinyl chloride copolymers and vinyl acetate vinyl chloride terpolymers having molecular weight in the range 5,000 to 70,000 are preferred. Vinyl acetate vinyl chloride copolymers and vinyl acetate vinyl chloride terpolymers having molecular weight in the range 15,000 to 50,000 are even more preferred. Examples of preferred polymers that are useful in the present invention include, but are not limited to, the solution vinyl resins sold under the commercial name of UCAR by Union Carbide, Bound Brook, New Jersey. A variety of grades vinyl resins are sold under this name and include UCAR SOLUTION VMCA, VMCCA, VMCH, VROH, VYHH and VYHD. An example of a preferred urea aldehyde polymer includes, but is not limited to, LAROPAL A 81 resin, sold by BASF Corporation in Charlotte, NC.

The variety of grades of suitable polymeric hyperdispersants includes DISPERBYK 116, DISPERBYK 140, SOLSPERSE 17000, SOLSPERSE 20000, SOLSPERSE 24000, SOLSPERSE 32000, SOLSPERSE 34750, EFKA 4008, EFKA 4009, EFKA 4046, EFKA 4047, EFKA 4048, EFKA 4520, EFKA 4010, EFKA 4050, EFKA 4055, EFKA 4400, EFKA 4401, EFKA 4403, EFKA 4530, EFKA 4560. Among these preferred polymeric hyperdispersants, even more preferred are SOLSPERSE 24000, SOLSPERSE 20000, EFKA 4050, EFKA 4055. Examples of preferred polymeric dispersing agents with pigment affinic groups include, but are not limited to, those sold by Avecia in Wilmington, Delaware under

the SOLSPERSE name and those sold by BYK-Chemie in Wellingford, CT under the DISPERBYK name. The variety of grades includes DISPERBYK 115, DISPERBYK 160, DISPERBYK 161, DISPERBYK 162, DISPERBYK 163, DISPERBYK 169, DISPERBYK 182, SOLSPERSE 5000, SOLSPERSE 12000 and
5 SOLSPERSE 22000, DISPERBYK 163, DISPERBYK 166, DISPERBYK 167 and DISPERBYK 168.

The ink-jet ink of the invention also can include a conductivity agent, such as a conductive salt. Examples of preferred conductivity salts include, but are not limited to potassium and ammonium thiocyanate, lithium nitrate, alkylammonium
10 salts. Preferred conductivity salts include, but are not limited to, tetrabutylammonium nitrate and tetrabutylammonium tetrafluoroborate. Especially preferred is tetrabutylammonium nitrate.

Various, known polymers and other viscosity modifying agents may be added to the set invention, as needed to adjust the viscosity. the preferred viscosity
15 range is 1.2 to about 20 centipoise at 25°C.

The surface tension and the wetting properties of a particular ink formulation of the set invention on the nozzle and substrate may be controlled by the small addition of surfactants or solvents.

Humectants may be added to the set ink-jet ink formulation to reduce the
20 evaporation of the ink from the nozzle. The humectant has a boiling point of greater than 100°C. Examples of humectants include, but are not limited to, glycerine and propylene glycol.

The ink-jet formulation of the set invention may contain additives for improving the compatibility and stability of the ink-jet formulation.

25 The ink-jet ink formulation in the present invention may be prepared by any known standard methods. The following examples illustrate the present invention and should not be construed as in any way limiting its scope. All percentages expressed herein are percentages by weight, based on the total weight of the ink composition of the present invention.

EXAMPLES	1	2	3
	(%w/w)	(%w/w)	(%w/w)
Methyl Ethyl Ketone	79.5	80.0	77
Pigment Dispersion 1 (*A)	16.4	12.6	-
Pigment Dispersion 2 (*B)	-	-	13.5
5 Pigment Dispersion 3 (*C)	-	1.4	1.5
UCAR Vinyl VROH (Union Carbide)	-	-	3.5
Tetrabutylammonium nitrate (Alfa Aesar)	1.4	1	1.5
ERL-4221 (Union Carbide)	0.1	0.1	0.1
DISPERBYK-163 (BYK-Chemie)	1.8	4	2
10 2,4-pentanedione (Aldrich)	0.8	0.9	0.9

*A 50% Pigment Orange 64/UCAR Vinyl VYHD dispersion from Akrochem

*B 50% Pigment Orange 64/UCAR Vinyl VROH dispersion from Akrochem

*C 50% Pigment Red 254/UCAR Vinyl VYHD dispersion from Akrochem

The above ink formulations were prepared and tested on a variety of black and white colored substrates. The inks were opaque and showed up clearly on white and black substrates. The adhesion of the inks as defined by the standard tape test was satisfactory. Printer stability and reliability tests were performed in an ink-jet printer. The ink-jet inks performed satisfactorily with no clogging of nozzles or blockage of filters. The settling properties of the inks were satisfactory. No settling of the pigment was obtained when aged at 60°C for 1 month or stored at room temperature for 1 year. In order to improve the opacity of the ink further in this set invention, titanium dioxide or other white pigments may be added. This particular modification of the set invention may lead to settling of the pigment. The ink can be used reliably in an ink-jet printer, which is fitted with a mechanical device to keep the pigment suspended in the ink.

EQUIVALENTS

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the

5 following claims.

CLAIMS

What is claimed is:

1. An ink-jet ink, comprising:
 - a) a colorant selected from the group consisting of Pigment Orange 16
5 and Pigment Orange 64;
 - b) a dispersant selected from the group consisting of polymeric
hyperdispersants and polymeric dispersing agents with pigment-
affinic groups;
 - c) a polymer; and
 - 10 d) a solvent.
2. An ink according to Claim 1, wherein the colorant is present in an amount in
a range of between about 2% and about 40% by weight of the ink.
3. An ink according to Claim 1, wherein the solvent is present in an amount up
to about 90% by weight, the pigment is present in an amount up to about
15 40% by weight and the polymer is present in an amount up to about 30% by
weight.
4. An ink according to Claim 3, wherein the solvent is selected from the group
consisting of lactates, esters, alcohols, ketones, acetates, hydrocarbons,
lactones, sulfones, glycols and glycol ethers.
- 20 5. An ink according to Claim 1, wherein the solvent includes 2-pyrrolidinone.
6. An ink according to Claim 1, wherein the solvent includes a substituted
pyrrolidinone.

7. An ink according to Claim 1, wherein the solvent includes a dialkylether of ethylene glycol.
8. An ink according to Claim 1, wherein the solvent includes diacetone alcohol.
9. An ink according to Claim 1, further including a conductivity agent.
- 5 10. An ink according to Claim 1, further including an additional pigment, said additional pigment selected from the group consisting of orange, red or brown pigment.
11. An ink according to Claim 1, wherein said pigment is dissolved in the solvent of the ink.
- 10 12. An ink according to Claim 1, wherein said ink is opaque on both black and white substrates.
13. An ink, comprising 1-5% by weight of a conductivity agent.
14. An ink according to Claim 13, wherein the conductivity agent is selected from the group consisting of potassium, ammonium thiocyanate, lithium
15 nitrate and alkylammonium salts.

INTERNATIONAL SEARCH REPORT

In tional Application No

PCT/US 00/10078

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 753 552 A (TOYO INK MFG CO) 15 January 1997 (1997-01-15) page 4, line 8 page 6, line 58 -page 7, line 2 page 6, line 27-33 page 7, line 8-19	1-4, 6, 7
X	EP 0 799 870 A (TOYO INK MFG CO) 8 October 1997 (1997-10-08) page 3, line 20-32 page 3, line 46, 47 page 3, line 57 -page 4, line 1 page 4, line 16-24	1-4
X	GB 2 325 670 A (STAEDTLER FA J S) 2 December 1998 (1998-12-02) page 3, paragraphs 6, 7	13, 14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

13 July 2000

Date of mailing of the international search report

25/07/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Miller, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/10078

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0753552	A	15-01-1997	KR 204380 B	15-06-1999
			US 5716435 A	10-02-1998
			WO 9623032 A	01-08-1996
EP 0799870	A	08-10-1997	JP 9268266 A	14-10-1997
			US 5772746 A	30-06-1998
GB 2325670	A	02-12-1998	DE 19722546 A	03-12-1998
			US 5935310 A	10-08-1999